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Molecular orbital study of torsional potentials, physicochemical properties and electronic spectra of methyl acrylate in different electronic states

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Abstract : A systematic study of the possible conformations of methyl acrylate and their stabilities in the ground (S_0) and first excited (S_1) electronic states has been undertaken using *ab initio* and MNDO(AM1) molecular orbital techniques by plotting potential energy curves Methyl acrylate was considered as a three rotor system having internal rotation about C–C and C–O single bonds with the possibility of hindered rotation of the methyl group. Four stable conformers Cc, Tc, Ct and Tt have been identified in the S_0 state in increasing order of energy with methyl group having staggered conformation with respect to carbonyl group in each case. The enthalpy difference between the two most stable conformers Cc and Tc in the S_0 state is 0.425 kcal/mol, well within the experimental range 0 43 ± 0.20 kcal/mol, and reduces to 0.325 kcal/mol in the S_1 state Unlike acrolein and other conjugated compounds, the conformations remain unchanged on $n\pi^*$ excitation. Geometries of the stable conformers in the two states have been optimized using 4–31 G extended basis set The barrier to internal rotation about the C–O bond in S_0 state is larger than that about the C–C bond and further increases in the S_1 state. Complete Mulliken population analysis has been carried out in the two electronic states to identify the possible resonance structures in the S_1 state. A theoretical assignment has been provided in CNDO/2 approximation to the electronic transitions in Cc and Tc conformers and compared with experimental results.

Keywords Molecular orbital calculations, conformation, methyl acrylate

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1. Introduction

α,β-Unsaturated carbonyl compounds such as aldehydes, ketones, carboxylic acids and esters have been subjects of detailed investigation by spectroscopic and quantum chemical techniques. It is found that while some of such compounds like acrolein [1,2] methyl vinyl ketone [3,4] *etc* may exist in *s-cis* and *s-trans* conformations, with the *s-trans* form being more stable than *s-cis*, the situation is less certain in the case of methyl acrylate. Although several studies of vibrational spectra of methyl acrylate [5,6] have shown preference for the *trans* conformer, microwave [7] and quantum chemical [8] studies have predicted the *s-cis* conformer to be more stable. No systematic study of the possible conformations of methyl acrylate and their stabilities in the ground (S_0) and first excited (S_1) $n\pi^*$ electronic states has been reported. Also, no theoretical assignments have been provided to the electronic spectra of the molecule. The present work intends to fill this gap. We report the results of our molecular orbital studies within the extended basis *ab initio*, MNDO (using AM1 Hamiltonian) and CNDO/2 frame work on the molecular geometry and potential energy curves, thermodynamic and physicochemical properties of the electronic ground and first excited states. Electronic transitions have been explained on the basis of CNDO/2 calculations involving configuration interaction between singly excited electronic states.

2. Method of calculation

Methyl acrylate (Figure 1) was considered as a three rotor system in which internal rotation may take place about C1–C2 and C2–O6 single bonds connecting completely asymmetric moieties $CH{=}CH_2$ and $O{=}COCH_3$ and $O{=}CCHCH_2$ and OCH_3, respectively and also a rotation of

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the methyl group about O6–C9 single bond. A number of conformations may, therefore, theoretically arise for the molecule due to rotation about the three bonds. In order to obtain potential energy curves for asymmetric torsion about C1–C2 and C2–O6 bonds in the electronic states S_0 and S_1 in the AM1 approximation, the dihedral angles ϕ(C3C1C2O4) and ϕ (O4C2O6C9) were changed from 0° to 360° in the intervals of 20° (intervals of 10° at turning points).

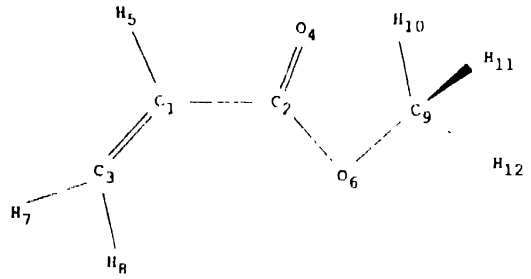

Figure 1. Numbering of atoms of methyl acrylate

Three-fold potential function of internal rotation of methyl group about O6–C9 bond was obtained by changing the dihedral angle ϕ (C2O6C9H10) in intervals of 20° for each of the stable conformations corresponding to potential minima on rotation about the C1–C2 and C2–O6 bonds. Torsional potential analysis was conducted after optimizing molecular geometry at each stage of rotation by using BFGS [9] method. Fully optimized geometries of the possible stable conformers were also obtained using 4-31 G basis sets. Electronic transitions and oscillator strengths were calculated in the CNDO/2 approximation using computer program CNDUV 99 [10] after taking into account configuration interaction between singly excited states. *Ab initio* Hartree Fock calculations with 4–31G basis set and MNDO (AM1) calculations were done using computer program GAMESS [11] and MOPAC ver. 6.0 [12], respectively.

3. Conformational notations

The notations used in this paper for conformers of methyl acrylate are analogous to those used previously by us for substituted propanal [13]. The conformers with respected dihedral angle ϕ(C3C1C2O4) are denoted by a capital C (*s-cis* or *syn*, ϕ = 0°) or T (*s-trans* or *anti*, ϕ = 180°). Rotation of the CH_3 group about O6–C9 bond may give rise to either eclipsed or staggered conformations relative to the carbonyl group. However, in the present case, only staggered conformations are found to be more stable and so no separate notation is used for the purpose. Conformations with respect to the dihedral angle ϕ(C2O6C9H10) are represented by the lower case letter *c* (*cis* or *syn*, ϕ = 0°) or *t* (*trans* or *anti*, ϕ = 180°) following the capital letters C or T.

4. Results and discussion

4.1. Conformational studies :

Potential energy curves for rotation about the C1–C2 bond for the ground (S_0) and excited (S_1) electronic states, with a *cis* conformation for the ester group, are given in Figure 2.

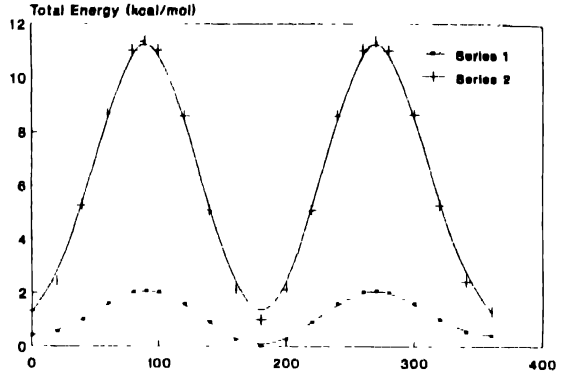

Figure 2. Potential energy curves of methyl acrylate for rotation about the C1–C2 bond in states S_0 (series 1) and S_1 (series 2). ϕ(O4C2O6C9) = 0° and ϕ(C2O6C9H10) = 60°. The abscissa is the angle of rotation θ about C1–C2 bond relative to *trans* (T) conformation for which the dihedral angle ϕ(C4C2C1C3) = 180° The ordinates for series 2 are shifted by 1 kcal/mol with respect to series 1

It may be seen that in both the states, the molecule has two potential minima at ϕ(C3C1C2O4) = 0° and 180° corresponding to the *s-trans* and *s-cis* conformations; the later being more stable than the former. Potential energy curves for rotation about the C2O6 bond in each of the above conformations are given in Figure 3. The corresponding

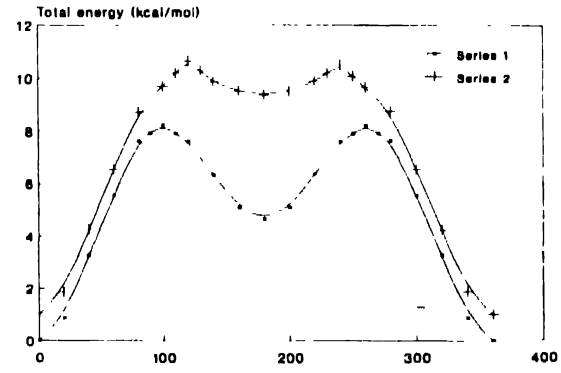

Figure 3. Potential energy curves for rotation about the C2–O6 bond for the *cis* (series 1) and *trans* (series 2) conformations of the acrolyl group in the S_0 state The abscissa is the angle of rotation θ about the C2–O6 bond relative to the dihedral angle ϕ(O4C2O6C9) = 0° The ordinates for series 2 are shifted by 1 kcal/mol with respect to series 1 Dihedral angle ϕ(C2O6C9H10)

curves for the S_1 state are given in Figure 4. These potential energy curves also show two energy minima corresponding to ϕ(O4C2O6C9) = 0° and 180°. Thus, as per the notations used, the molecule may exist in four stable rotameric forms

Cc, Ct, Tc and Tt, both in the S_0 and S_1 states. Further, it was found that in each of the above conformers, the methyl group has a staggered conformation relative to the carbonyl group as the total energy of the molecule reduces by about 1.0 kcal/mol on rotating methyl group from an eclipsed to staggered conformation.

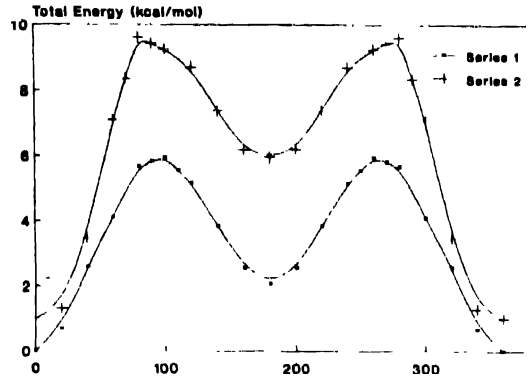

Figure 4. Potential energy curves for rotation about the C2–O6 bond for the *cis* (series 1) and *trans* (series 2) conformations of the acrolyl group in the S_1 state. The abscissa is the angle of rotation θ about the C2–O6 bond relative to the dihedral angle ϕ(O4C2O6C5) = 0°. The ordinates for series 2 are shifted by 1 kcal/mol with respect to series 1. Dihedral angle ϕ(C2O6C9H10).

The relative energies of the various stable conformers of the molecule in the S_0 and S_1 states are given in Table 1. It may be seen that in the electronic ground state the energies of the four conformers follow the sequence Cc, Tc, Ct and Tt in an increasing order. Out of the four potential wells corresponding to these conformers only three, corresponding to Cc, Tc and Ct, have sufficient depths of 8.208, 9.648, 3.574 kcal/mol, while the Tt conformer has a shallow potential well of about 1.274 kcal/mol depth. Hence, during a photoisomerisation experiment at low temperatures one may detect the presence of only three stable conformers. No such experimental study on methyl acrylate has, however, been reported. As in the S_0 state, it is found that in the excited S_1 state as well the molecule can exist in four stable conformations Cc, Tc, Ct and Tt, in increasing order of energy. This situation is different from that prevailing in other similar compounds like acrolein [2] and methyl vinyl ketone [4], where the $n\pi^*$ transition reverses the stability order of the molecule from *trans* to *cis*. Further, unlike the ground state, the Tt conformer in the excited state of methyl acrylate may be more stable as it lies at the bottom of a deep potential well of 3.625 kcal/mol height.

The enthalpy difference between the Cc and Tc conformers in the S_0 is 0.425 kcal/mol (Table 1), which lies within the range 0.43 ± 0.20 kcal/mol reported from experimental measurements [5,14–16]. The enthalpy difference between Cc and Ct and Tc and Ct conformers are 4.635 and 4.212 kcal/mol, respectively. However, no experimental results are available for these conformers to confirm our findings. The potential barrier between Cc and Tc conformers arising out of rotation about the C1–C2 bond is found to be 2.087 kcal/mol. This is much less than the barrier (8.208 kcal/mol) due to rotation about the C2–O6 bond, *i.e.* between the Cc and Ct conformers. Similar results have been reported for saturated acids and esters [17] from experimental measurements [18] where the rotational barrier about the C–O bond is estimated to be about 10–15 kcal/mol. As compared to the S_0 state, $n\pi^*$ electronic transitions tends to reduce the enthalpy difference between the four conformers Cc, Tc, Ct and Tt in the S_1 state (Table 1), while increasing their rotational barriers. This adds to the stability of these conformers. The rotational barrier between the Cc and Tc conformers, which are most stable in the ground state, increases from 2.087 to 10.363 kcal/mol in S_1 state.

Table 1. Total energy, enthalpy difference, rotational barrier and ionisation potential of different conformers of methyl acrylate in ground (S_0) and excited (S_1) state in AM1.

Ground state (S_0)		Excited state (S_1)	
Conformation	Total energy (kcal/mol)	Conformation	Total energy (kcal/mol)
Cc	0 0[a]	Cc	0 0[b]
Tc	0.425	Tc	0.325
Ct	4 635	Ct	2 083
Tt	8 798	Tt	5 302
	Enthalpy difference (kcal/mol)		
Cc–Tc	0 425	Cc–Tc	0 325
Cc–Ct	4 635	Cc–Ct	2 083
Tc–Ct	4 212	Tc–Ct	1 758
	Rotational barriers (kcal/mol)		
Ct/Tc	2 087	Cc/Tc	10.363
Tc/Ct	1 622	Tc/Cc	10 038
Cc/Ct	8 208	Cc/Ct	5 961
Ct/Cc	3 574	Ct/Cc	3.878
Tc/Ct	9.830	Tc/Ct	15 999
Ct/Tc	11 782	Ct/Tc	14 241
		Tc/Tt	8 602
		Tt/Tc	3.625
	Ionisation potential (eV)		
Cc	11 094	Cc	4 851
Tc	11 079	Tc	4.812
Ct	11 013	Ct	4 903
Tt	11 003	Tt	5 039

[a]absolute value −28496 210 kcal/mol
[b]absolute value −28417 199 kcal/mol

4.2. Optimized geometries .

Completly relaxed optimized geometries of the four stable conformers Cc, Tc, Ct and Tt of methyl acrylate were obtained both for the electronic ground (S_0) and excited (S_1) states within the AM1 framework. These were further improved in case of the S_0 state by extended basis 4–31 G *ab initio* Hartree Fock calculations and are reported in Table 2. It may be seen that both the semi-empirical and *ab initio* methods give comparable geometries which differ by not more than 0.003 Å in bond length and 3° in bond angles. The geometries of Cc and Tc conformers are very close to those reported by Garcia *et al* [8], differing from later by an average of 0 001 Å and 0.5° in bond lengths and bond angles, respectively. The geometries for the Ct and Tt conformers have not been reported earlier.

4.3. Methyl torsion :

Three-fold potential functions for the internal rotation of the methyl group about O6–C9 bond in the two most stable conformers Cc and Tc of methyl acrylate, have been calculated for the S_0 and S_1 states. Total energy of the conformers on methyl rotation were obtained and plotted against the dihedral angle ϕ(C2O6C9H10). Since the potential energy curves for both the conformers in the ground and excited states are identical, the curves for the Cc conformer alone in the S_0 and S_1 states are shown in Figure 5. It is found that the minimum of the potential curve in all these cases lies at ϕ = 60°, corresponding to the staggered conformation of the methyl group with respect to the carbonyl bond. The barrier to internal rotation of the methyl group in the Cc and Tc conformers in the S_0 electronic state is found to be 0.826 and

Table 2. Optimized geometries of different conformers of methyl acrylate in ground (S_0) and excited (S_1) states, bond lengths are given in Angstroms and angles in degrees

	Ground state								Excited state			
Internal Coordinates	Cc AM1	Cc 4-31G	Tc AM1	Tc 4-31G	Ct AM1	Ct 4-31G	Tt AM1	Tt 4-31G	Cc AM1	Tc AM1	Ct AM1	Tt AM1
C1-C2	1 467	1 466	1 466	1.466	1 468	1 478	1 468	1 482	1 423	1 426	1 428	1 425
C1=C3	1 333	1 318	1 332	1 318	1 334	1 319	1 329	1 319	1 436	1 348	1 350	1.339
C2=O4	1 234	1 211	1 234	1 211	1.234	1 205	1 236	1.206	1 240	1 232	1 239	1 230
C1-H5	1 101	1 070	1 103	1 070	1.100	1.068	1 110	1 070	1 111	1 106	1.105	1.117
C2-O6	1 371	1 343	1.372	1 343	1 375	1 349	1 372	1 346	1 378	1 389	1.378	1 393
C3-H7	1 098	1 070	1 099	1 071	1 098	1 071	1 102	1 071	1 115	1 114	1 114	1.116
C3-H8	1 004	1 071	1.099	1 070	1 101	1 071	1 095	1 066	1 115	1 114	1.114	1 116
O6-C9	1 427	1 442	1 427	1.443	1 420	1 434	1.415	1 431	1.424	1 421	1 416	1.407
C9-H10	1 116	1 077	1 116	1 077	1 117	1.079	1.117	1 078	1 116	1 116	1.118	1 121
C9-H11	1 116	1 077	1 116	1 077	1 117	1.079	1 117	1 078	1 118	1 118	1.119	1 121
C9-H12	1 117	1 073	1.117	1 074	1 120	1 074	1 121	1.074	1 118	1 118	1 117	1 210
C2C1C3	121 5	121 1	124 0	123 9	121 1	120.3	131 0	131 2	126 4	124 9	124.0	132 4
C1C2O4	129 2	125 7	127 6	123 7	126 6	123 0	122 6	118.6	128 0	130 4	126.9	129.1
C2C1H5	115.2	116.0	113 0	113 7	117.2	118 9	109.9	109 6	115.4	114.6	118.6	111 9
C1C2O6	112.8	111.9	114 7	114.1	121 7	118 1	127 1	123 5	112 9	111.0	120.9	119 3
C1C3H7	121 8	121 5	121.7	121.1	122.0	121 5	120 1	119.4	123 6	123.6	123 5	123 9
H8C3C1	122 3	121 0	122 5	121.5	122.1	120.8	126.2	125 2	123 6	123.6	123 4	123 9
C2O6C9	116 5	119 7	116 5	119 5	118.7	126 2	121.0	130 8	117 8	118.2	118.4	118 0
O6C9H10	109 9	110.0	109 9	110 0	110.7	111.1	110.7	111.1	112.8	112.4	110.7	111 0
O6C9H11	109 9	110 0	109 9	110 0	110 7	111 1	110 8	111 1	106.1	106 4	103.8	111 2
O6C9H12	103 6	105 2	103 6	105.2	103 6	104 9	103 4	104 5	106 0	106.2	110.7	104 5
C3C1C2O4	0 0	0 0	180 0	180 0	0 0	0 0	180 0	180.0	0.202	179 9	0 393	179 4
O4C2C1H5	180 0	180 0	0 0	0.0	180.0	180 0	0.0	0 0	179 8	0 120	178.4	0.285
O4C2O6C9	0.0	0 0	0 0	0 0	180.0	180 0	180.0	180.0	0.185	0.248	179.6	179 1

0.825 kcal/mol, respectively, which decreases to 0.794 and 0.643 kcal/mol, respectively in the S_1 state. The calculated heights of rotational barrier and their reduction on electronic

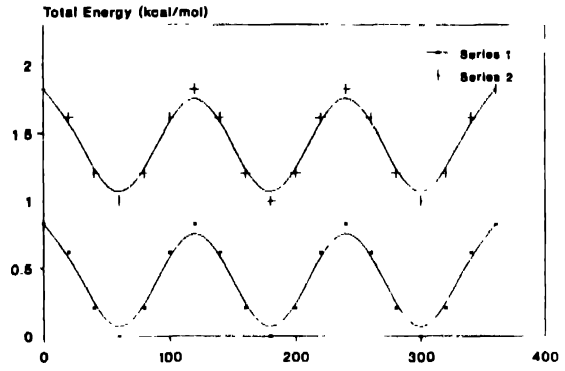

Figure 5. Potential energy curves for methyl rotation about O6–C9 bond in Cc conformer of methyl acrylate in the ground (series 1) and first excited (series 2) electronic states The abscissa is the angle of rotation θ relative to the dihedral angle ϕ(C2O6C9H10) = 0°. The ordinates for series 2 are shifted by 1 kcal/mol with respect to series 1.

excitation are typical of the methyl group in aldehydes [19] and ketones [4] and indicate an almost free rotation of the group. The potential energy curves in all cases show a C_{3v} symmetry for methyl group.

4.4. Population densities, dipole moments and ionisation potentials :

Mulliken population analysis was conducted on the four possible stable conformers Cc, Tc, Ct and Tt of methyl acrylate in the S_0 and S_1 states. The results are given in Table 3. A strong correlaton is found to exist between the bond orders and bond lengths of the various conformers in both the electronic states as may be seen from Tables 2 and 3. An increase/decrease in the bond length on electronic excitation is accompanied with a corresponding decrease/increase in bond orders of all bonds like C1–C2, C1=C3, C2=O4, C2–O6 and O6–C9. The electronic excitation tends to significantly reduce the bond orders of the C1=C3, C2=O4 and C2–O6 bonds, while increasing the value for C1–C2 bond. This indicates a significant charge redistribution and resonance effects within the acrolyl group and a major contribution made by resonance structure of the type :

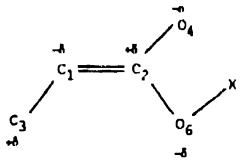

Table 3. Atom and bond population (q-values) and dipole moments for different conformers of methyl acrylate in ground and excited states in AM1

Atom or bond	Ground state				Excited state			
Population	Cc	Tc	Ct	Tt	Cc	Tc	Ct	Tt
qC1	6 1913	6 1917	6 2409	6 2092	6 8118	6 8132	6 8648	6.8571
qC2	5 6721	5.6709	5.6739	5 6745	5 6842	5 6820	5 6834	5 6777
qC3	6.1309	6.1289	6 1143	6 1536	5 3788	5.3744	5 3824	5 4455
qO4	8 3545	8 3492	8 3049	8 3005	8 4533	8 4368	8.4009	8 3849
qH5	0.8456	0 8445	0.8602	0.8425	0 7757	0 7783	0 7911	0 7668
qO6	8 2755	8.2826	8.2510	8 2495	8 2932	8 3007	8.2497	8 2568
qH7	0.8749	0.8769	0.8768	0 8740	0 9037	0 9042	0 9028	0 9076
qH8	0.8631	0 8646	0.8589	0 8781	0.9037	0 9043	0 9028	0 9076
qC9	6 0626	6 0615	6.0720	6 0710	6.0705	6.0740	6 0728	6 0609
qH10	0.9153	0 9147	0 9293	0 9294	0.8900	0.8938	0 9318	0 9277
qH11	0 9154	0 9148	0.9293	0 9292	0.9179	0 9196	0 8856	0.9259
qH12	0 8987	0.8998	0.8887	0.8885	0 9171	0 9187	0.9320	0.8814
qC1–C2	0.9576	0.9555	0.9484	0 9444	1.1760	1 1694	1 1311	1.1318
qC1=C3	1.9285	1.9324	1.9272	1.9395	1 1793	1 1706	1 1745	1.2073
qC2=O4	1.7835	1 7912	1.8189	1 8229	1.6259	1.6428	1.6721	1 6898
qC2–O6	1.0220	1 0164	1.0059	1 0060	0 9768	0 9622	0 9775	0 9549
qO6–C9	0.9521	0.9510	0 9689	0 9687	0.9559	0.9610	0.9741	0.9830
μ (Debye)	1.60*	2.32	4 43	4 85	5.99	7 64	7.82	9.97

*Experimental value = 1 75D in liquid phase [20]

Table 4. Electronic transitions in Cc and Tc conformers of methyl acrylate in CNDO-CI(S) approximation.

Cc			Tc		
Experimental λ_{nm} (log ε)	Calculated λ_{nm} (log ε)	Assignment	Experimental λ_{nm} (log ε)	Calculated λ_{nm} (log ε)	Assignment
296[a]	295 8 (0 80)	n-π^*	–	306.4 (0.80)	n-π^*
240[a]	231 8 (4 34)	π-π^*	–	227.9 (4 53)	π-π^*
194 (4 0)[b]	197.0 (4 06)	π-π^*	–	194 3 (3.84)	π-π^*

[a]In alcoholic solution, [b]In heptane solution

The calculated dipole moments of Cc, Tc, Ct and Tt conformers in AM1 approximation in S_0 state are 1.60 D, 2.23 D, 4.43 D and 4.85 D, respectively. Our calculated value for the Cc conformer is very close to the experimental value 1.75 D [20] in the liquid phase. Extended basis 4–31G calculations provide slightly higher values for all these dipole moments at 1.65 D, 2.66 D, 5.57 D and 6.02 D, respectively. Electronic excitation tends to increase the dipole moments of all the four conformers to 5.99 D, 7.64 D, 7.82 D and 9.97 D, respectively, thereby making the S_1 state to be more polar than S_0 state. It may further be seen from Table 3 that while a rotation about C1–C2 bond brings about a small change in dipole moments of the Cc and Tc conformers, rotation about C2–O6 bond changes the value significantly in Tc and Tt conformers. No experimental data is available in the literature for the dipole moments of these conformers in the excited state S_1.

4.5. Electronic transitions

The electronic transition energies and oscillator strengths for two major conformers Cc and Tc of methyl acrylate were calculated in the CNDO/2 approximation after taking into account configuration interaction between singly excited states *i e.* at the CNDO-CI(S) level. These are given in Table 4. Based on experimental measurements Ungnade and Ortega [21] reported two absorption peaks in the near uv-spectrum of methyl acrylate at 295 nm and 240 nm in alcoholic solution while Petukhov *et al* [22] reported an absorption band at 194 nm (log ε = 4.0) in heptane. As may be seen from Table 4, these peaks lie close to the calculated electronic transitions at 295.8 nm, 231.8 nm and 197.0 nm in case of the most stable Cc conformer. While the 295.8 nm band may be assigned to a forbidden low intensity n-π^* transition, the other two bands at 231.8 nm and 197.0 nm are strong bands with log ε value of 4.34 and 4.06, respectively and may be assigned to π-π^* transitions. The corresponding bands in Tc conformer appear at 306.4 nm, 227.9 nm and 195.3 nm, with log ε values of 0.80, 4.53 and 3.84, respectively, and lie close to the absorption peaks of the Cc conformer. No experimental data is however, available for the Tc conformer.

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